Journal of Alloys and Compounds 712 (2017) 425–430

Contents lists available at ScienceDirect

Journal of Alloys and Compounds

journal homepage: http://www.elsevier.com/locate/jalcom

A self-powered ultraviolet photodetector driven by opposite Schottky junction

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ARTICLE INFO

Article history:
Received 8 March 2017
Received in revised form
10 April 2017
Accepted 13 April 2017
Available online 14 April 2017

Keywords:
Self-powered
Schottky junction
Ultraviolet photodetector
Metal
Semiconductor

ABSTRACT

In this study, we demonstrate a relatively independent UV photodetector which is composed of one layer of Au/Ag/Pt metal nanoparticles sandwiched between two layers of n-type TiO_2 semiconductor nanorods. Different from most reported Schottky junction based UV photodetectors, it can be driven only by two opposite Schottky junction in the sandwich structure, but no need for any external power supply except UV light when it works. Moreover, it displays high responsivity and fast response speed at the same time, giving a bright prospect for self-powered UV photodetectors.

1. Introduction

Ultraviolet (UV) photodetectors (PDs) have been paid more and more attentions, due to their important applications in scientific, military, and commercial fields, including UV imaging, flame detection, ozone layer monitoring, missile warning system, etc [1,2]. The physical mechanism of photodetection is the generation of electron–hole pairs by the optical absorption of incident photons. The obtained electron–hole pairs are then separated by a potential difference, and thus photocurrent is formed. In traditional UV PDs, it requires additional power supply to provide the potential difference, which makes the overall circuitry heavy and uneconomical in the current energy scenario [3,4]. Thus, self-powered UV PDs driven by a built-in potential difference have been emerging and been attracting considerable interests. This kind of UV PDs could be operated without any power supply, which makes them have some special advantages, such as saving energy, small device size and suitable use in extreme conditions [5,6]. Basically, according to the cause of built-in difference, self-powered UV PDs can be divided into three types: Schottky junction type [7,8], p-n junction type [9,10] and photoelectrochemical cell (PECC) type [11,12]. PECC self-powered UV PDs are evolved from a photoanode/electrolyte/counter electrode structure, which is similar with other PEC devices. Although this kind of PDs has exhibited high performances of UV photodetection, electrolyte leakage and device sealing limits its applications especially in portable devices. A ZnO/PANI/ZnO UV PD has been reported to be powered by two opposite p-n junction, and a photosensitivity ($>10^5$) was obtained by assistant of PSS [13]. Compared to the p–n junction, the Schottky junction features as facile fabrication processes and material universality [14]. In Particular, it can be formed with basically any semiconductors, such as the most available semiconductors of TiO_2 and ZnO.

It has been demonstrated that Schottky junction existing between the interface of metal and semiconductor could drive a photodetector without any external power supply [7,8]. However, there are still some issues existing in these devices, such as the complicated preparation process and the poor electrode contacts between metal and semiconductor. Particularly, as we know, few UV PDs based on ZnO or TiO_2 are reported to be powered only by Schottky junction, although the two semiconductors are in virtues of wide direct band gap, low defect density, and strong radiation

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http://dx.doi.org/10.1016/j.jallcom.2017.04.129
0925-8388/

hardness for use in UV photodetection [15]. In fact, until now, most Schottky junction based UV PDs are based on the metal-semiconductor-metal (MSM) structures, which are controllable, stable, and can be fabricated easily. Nevertheless, the MSM PDs always require an external power source as the driving force to generate photocurrent due to their two symmetric Schottky contacts connected back to back on a planar surface. X. Zhao et al. fabricated a UV PD based on Au/ZnO/Au structure, and obtained a high responsivity of 4.9×10^6 A W^{-1} at a high voltage of 5 V. However, the rising and decay time is 6.3 s and 26.3 s, respectively, which are too slow [16]. X. Kong et al. reported a MSM TiO_2 UV detectors with Ni electrodes, and also acquired a high responsivity of 889.6 A W^{-1} at external voltage of 5 V. Similarly, the slow decay time of 11.43 is not acceptable [17]. J. Xing et al. presented a MSM TiO_2 UV detectors with Ag electrodes, and exhibited a responsivity of 3.63 A W^{-1} as well as an ultrafast rising/decay time of 8ns/150 ns [18]. However, the applied external voltage supply is as high as 10 V, which limited its further application. According to the previous reports, the existing Schottky junction based UV PDs are still confronted with a trade-off between responsivity and response speed. Even worse, they need to be powered by the applied bias. Therefore, it is crucial and highly desired to develop a new type of self-powered UV PDs with high performances.

In this work, by designing and preparing a sandwich-like structure consisting of one layer of Au nanoparticles and two layers of TiO_2 nanorods, we demonstrate a relatively independent UV PD which works without any external bias voltage except UV light. Due to the design of two opposite Schottky junctions in the device, the proposed UV PD exhibits a high photoresponsivity together with fast response speed at zero bias.

2. Material and methods

2.1. Hydrothermal growth of TiO_2 NRs arrays

In a typical synthesis [19], 26 mL of deionized water was mixed with 26 mL of hydrochloric acid (37% by weight) under stirring for 5 min. Then a certain amount of titanium isopropylate (TIP) was added dropwise and stirred for another 5 min. The precursor was transferred into a Teflon-lined autoclave (80 mL), and then two pieces of FTO (14 Ω cm^{-2}) glass were immersed into the solution at an angle against the wall with conductive side facing down. The hydrothermal reaction was carried out at 180 °C for 4 h in an electric oven. After synthesis, the autoclave was cooled to room temperature by flowing water, and the FTO glasses were taken out, thoroughly rinsed with deionized water, and dried in ambient air.

2.2. Deposition of Au (Ag and Pt) NPs on TiO_2 NRs

Au nanoparticles were prepared by in situ reduction assisting by UV light [20]. The TiO_2 NRs were firstly immersed in 1 mM HAuCl4 aqueous solution with PH value of 5 at room temperature for 30 min. Then the sample was directly illuminated with an 8 W portable mercury lamp (365 nm, 327.6 nW/cm^2) for 40 min. After that, the sample was rinsed with absolute ethanol and deionized water several times, and then was dried in air at room temperature for use. As for the deposition of Ag, the concentration of $AgNO_3$ precursor was 1 mM, but the PH value was adjusted to 3.5 by perchloric acid, the other reaction conditions were the same as those of Au. For the deposition of Pt, the 1 mM HPtCl6 methanol solution with PH value of 5 was used instead of aqueous solution. Before UV irradiation, Nitrogen was blowed into the reaction solution for 30 min to remove oxygen. The other reaction conditions were the same as those of Au.

2.3. UV PD assembly

The UV PD was assembled by putting together two pieces of TiO_2 NRs/Au NPs with Au face to face. The active area of the PD is 0.4 cm^2. The measurements of the current-voltage (*I-V*) characteristics and the photoresponse of the devices were conducted with an IviumStat Electrochemical Station under irradiation of a portable mercury lamp (Spectroline, ENF-280C/FA) with 365 nm wavelength. The UV light intensity was obtained by optical power meter (Newport, 1916-R).

3. Results and discussion

TiO_2 nanorods grown on Fluorine tin oxide tin oxide (FTO) glass are shown in Fig. 1(a). It is clearly seen that vertically aligned TiO_2 nanorods on FTO glass exhibit uniform density and size distribution. Furthermore, the average diameter of TiO_2 nanorods is 100 nm, and the length is as high as 2.39 μm, as shown in the inserted SEM image. The large aspect ratio provides a more efficacious electron transport pathway for photogenerated electrons. From Fig. 1(b), it is obvious that Au nanoparticles are deposited on TiO_2 nanorods and the average diameter is about 30 nm, which is further demonstrated by the EDX image in Fig. 1(c).

By putting together two pieces of TiO_2/Au on FTO glass with Au face to face, the TiO_2/Au/TiO_2 sandwich-like structure is formed, in which two layers of TiO_2 nanorods are separated by one layer of Au nanoparticles, as illustrated in Fig. 2. The FTO glass also served as a common substrate for directly connecting the TiO_2 nanorods with an external circuit.

As is well known, the work function of semiconductor is generally smaller than that of metal, therefore, when the metal and the semiconductor (for example, n-type) contact with each other, the electrons will diffuse from the semiconductor into the metal to form a depletion zone. The direction of the inner electric field in the depletion zone is from semiconductor to metal. In our design, the Schottky junction is formed between TiO_2 nanorod and Au nanoparticle, which is verified through the *I-V* characteristics of TiO_2 and Au, as shown in Fig. 3(a). In the dark, the rectifying ratio (defined as the ratio of photocurrent under the forward-bias to the photocurrent under the backward-bias) of TiO_2 nanorods/Au nanoparticles is about 57, indicating the formation of Schottky junction at the interface. Under the UV light illumination, there is a considerable enhancement in the photocurrent under the backward-bias, leading to an increase of 3200% of the rectifying ratio. Such a good Schottky junction can separate the photogenerated electrons and holes effectively, resulting in an impressive responsivity and response speed. In our designed TiO_2/Au/TiO_2 device, there are two opposite directional inner electric fields as shown in Fig. 3(b). When the sandwich-structured TiO_2/Au/TiO_2 device is irradiated with UV light from the bottom FTO glass, the electron-hole pairs are generated in the bottom depletion zone. Driven by the bottom inner electric field with the direction from TiO_2 to Au, the photoelectrons move through TiO_2 to the bottom FTO glass, and the photogenerated holes move toward the upper Schottky junction through Au nanoparticles layer. These holes accumulates in the upper area of the TiO_2 that is interfaced with Au, leading to an electropositive region, which is prone to attract electrons. As a result, the electrons will move from bottom to up through the external circuit, and then are injected into the TiO_2 nanorods on the up side of the device. Finally these electrons will shift to the upper depletion zone to neutralize the positive holes.

As shown in Fig. 4(a), a jump of ~100 nA was observed when the left 365 nm UV light was turned on, and the current immediately fell back to ~5 nA once the left UV light was turned off. The photosensitivity (defined as the ratio of the photocurrent to the